Electroactive Poly(aromatic amine) Films for Iron Protection in Sulfate Medium

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Polyaniline (PANi) and poly(1,5-diaminonaphthalene) (PDAN) films can be deposited on iron from aqueous sulfuric acid. The films exhibit electroactive properties similar to those of PANi and PDAN generated on platinum. Electrosynthesis performed in the presence of both monomers leads to a composite film which presents excellent adhesion properties on iron.

poly(1,5-diaminonaphthalene) (PDAN)

PDAN films can be deposited on iron electrodes by potential cycling. In order to obtain a rapid passivation of the electrode, a potential of 0.45 V was applied and then the electrode was dipped in the electrolyte. PDAN film formed on iron is thin, compact and adherent.

PANi films have also be grown on iron by cyclic voltammetry. Analysis of the films obtained after the first few scans seems to indicate that a passive metal oxide film is first formed on the iron surface, with polyaniline being deposited on top of it. After 20 minutes, a 3 μm thick dark green film is formed. This film is not adherent on iron.

In order to improve the film adherence, we have attempted to copolymerize 1,5-DAN and aniline. The CVs obtained during oxidation of 5.10^{-2} M aniline and 10^{-3} M 1,5-DAN on an iron electrode are presented in figure 1. In the first 20 mn of cycling the CVs are similar to that for PDAN growth alone: redox system I is observed at Epa = 0.5 V; Epc = 0.44 V (fig. 1a). Then two other systems appear: II at (0.56 V/0.51 V) and III at (0.81 V/0.74 V). Systems II and III indicate the growth of PANi (fig. 1b). These results indicate that at the beginning PDAN formation occurs, followed by the composite poly(ANi-DAN). The resulted film was characterized by CV, FTIR and XPS.

The composite film imparts a form of anodic protection for at least 9 days in pH 4 sulfate medium (fig. 2). The protection mechanism of the polymer layer was investigated using in-situ spectroelectrochemical techniques such as Raman and Infrared spectroscopies [1].

[1] A. Meneguzzi, M.C. Pham, J.C. Lacroix, B. Piro, A. Adenier, C.A. Ferreira and P.C. Lacaze, J. Electrochem. Soc., in press.

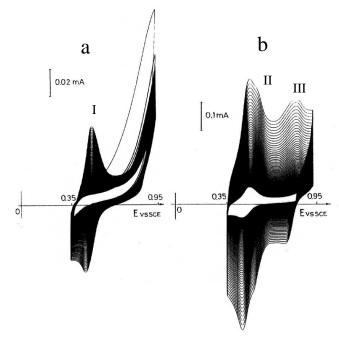
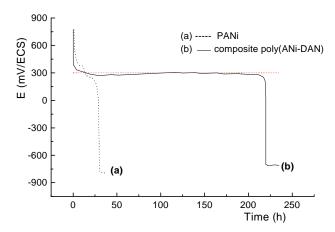


Figure 1: CVs at 50 mV s⁻¹ for the oxidation of 10^{-3} M DAN + 5.10^{-2} M aniline in 2 M H₂SO₄ on iron electrode (dia. 0.5 cm). a) first 20 mn of scanning b) following scans.



 $\begin{array}{c} \mbox{Figure 2: Open circuit potential } (V_{oc}) \mbox{ vs. exposure time} \\ \mbox{in 0.1 M} \ \ K_2SO_4(pH\ 4.0) \mbox{ for film- coated iron electrode} \\ \mbox{a) PANi.} \ \ \ \mbox{b) composite poly(ANi-DAN)} \end{array}$